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Combined Effects of Organic Reactivity and NMHC/NOx Ratio on Photochemical Oxidant Formation - A Modeling Study

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16. ABSTRACT

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COMBINED EFFECTS OF ORGANIC REACTIVITY AND NMHC/NO_x RATIO ON PHOTOCHEMICAL OXIDANT FORMATION—A MODELING STUDY

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Abstract—A modeling study was undertaken to assess the effect of organic reactivity on photochemical oxidant formation. A six-component hydrocarbon model was developed and tested against data collected in a smog chamber study of irradiated auto exhaust and oxides of nitrogen (NO_x) mixtures. The model was then adjusted to conditions that more closely approximated those of the urban environment. The adjusted model was used to assess the relative reactivity of various organic constituents when present in an urban-like air mass. Twelve organics were investigated in the study: ethane, propane, *n*-butane, ethylene, propylene, *trans*-2-butene, toluene, *m*-xylene, methanol, ethanol, formaldehyde and acetaldehyde. The findings of this study indicate that the reactivity of organics depends strongly on the hydrocarbon-to-NO_x ratio of the mix in which they are reacting. At low hydrocarbon-to-NO_x ratios, the organics investigated in this study displayed significantly different O_3-forming potential. At high hydrocarbon-to-NO_x ratios, however, all organics exhibited comparable O_3-forming potential.

Key word index: Organic reactivity, photochemical modeling, photochemical oxidants, photochemical reaction mechanisms, photochemical smog, smog chambers.

INTRODUCTION

The concept that different organics have different capabilities to produce photochemical oxidants was recognized 30 years ago by Haagen-Smit *et al.* (1953). This concept of organic reactivity has been subsequently verified in numerous smog chamber experiments in which different organics were irradiated with oxides of nitrogen (Brunelle *et al.*, 1966; Dimitriades and Joshi, 1977; Heuss and Glasson, 1968; Laity *et al.*, 1973; Wilson and Doyle, 1970). In these experiments, different organics gave rise to different ozone levels, and the organics were ranked by the investigators according to their ability to generate ozone. The fact that organics could be ranked in this fashion led the Los Angeles Air Pollution Control District to promulgate Rule 66 (County of Los Angeles, 1966). The primary emphasis of the Rule 66 approach was to limit the emissions of highly reactive organics more severely than the emissions of low-reactivity organics, thus concentrating more on changing the nature of the emissions than on reducing them. The U.S. Environmental Protection Agency, on the other hand, adopted an oxidant control strategy (Fed. Reg., 1977) that focused on the control of all organic emissions except for those few that had been shown to be so unreactive that they could not contribute significantly to O_3 formation under any circumstances. This approach led to a two-class reactivity scale: unreactive and reactive.

Much controversy still exists regarding the issue of reactivity and whether oxidant control strategies should be based on the selective control of the more reactive organics or whether all organics except those of negligible reactivity should be controlled. The intent of the modeling study presented here was to assess the relative reactivity of various organic constituents when present in an urban-like mix in an effort to determine if their reactivities are sufficiently different to render selective control of organics a viable approach to oxidant control.

REACTION MECHANISM

The reaction mechanism used in this study contained six hydrocarbon (HC) species: *n*-butane, ethylene, propylene, *trans*-2-butene, toluene and *m*-xylene. The inorganic reactions and rate constants and the detailed reaction schemes for ethylene, propylene and *m*-xylene were taken from Whitten *et al.* (1983). The toluene mechanism was obtained from Killus and Whitten (1982). Reactions for *n*-butane were taken from Whitten *et al.* (1980), and *trans*-2-butene chemistry was obtained from Atkinson and Lloyd (1984). The mechanisms for all six hydrocarbons have been extensively tested against data collected in both indoor and outdoor smog chambers. The composite mechanism for this 6-component HC and oxides of nitrogen (NO_x) system contained 169 reactions and 74 species.*

* Because of space limitations the mechanism has not been included here, but it is available from the author upon request.

Calculations were performed on a UNIVAC 1100 computer using either the CHEMK program written by Whitten and Hogo (1980) or a modified version of the Whitten and Hogo (1978) OZIPP program that enables the user to calculate O_3 isopleths for any given kinetics mechanism. Both programs use sparse matrix methods (Spellmann and Hindmarsh, 1975) to solve the differential equations according to the method of Gear (1971).

TESTING OF THE REACTION MECHANISM

The reaction mechanism was tested against smog chamber data in order to determine if an urban-like mix of organics could be apportioned among the six HC species that were treated explicitly in the mechanism. Smog chamber data of irradiated auto exhaust and NO_x mixtures, conducted by the Bureau of Mines (BOM), were used in this testing. In the BOM study, a 100-ft^3 aluminum chamber was charged with dilute auto exhaust mixed with varying amounts of added NO and NO_2. Non-methane hydrocarbon (NMHC) and NO_x reactants ranged from 0.2 to 5.0 ppmC and 0.08–1.4 ppm, respectively. The initial NO_2 concentration was adjusted to approximately 10% of the initial NO_x. The NMHC/NO_x ratios of the resulting mixtures ranged from 2.3 to 11.9. Chamber contents were irradiated for 6 h with a mixture of blacklights, blue lamps and sunlamps. A complete description of the experimental procedures and results obtained in this study are presented elsewhere (Dimitriades, 1970, 1972, 1977).

The chamber-dependent parameters used to model the BOM data are given in Table 1. The NO_2 photolysis rate and the rates of chamber dilution and dark decay of O_3 were measured in the BOM study. The pseudo-first order rate constant of 0.3 min^{-1} for the reaction of N_2O_5 with H_2O at 40% relative humidity corresponds to the upper limit for this reaction as reported by Morris and Niki (1973). Following the procedure adopted by Whitten *et al.* (1983), the reaction Wall → HCHO was used to simulate chamber contamination effects by assuming that the walls off-gas formaldehyde deposited in previous experiments. An initial concentration of nitrous acid was also included in the simulations to account for the formation of this species during the loading of smog chambers (Chan *et al.*, 1976). The radical source strength resulting from these latter two chamber-dependent parameters was very small, and including these radical sources had minimal effect on the predictions. The reported initial concentration of formaldehyde, which was the only aldehyde species measured in the BOM runs, was also included in the simulations. Acetaldehyde was taken to represent the remaining aldehyde content of the auto exhaust samples. Its molar concentration was assumed to be 75% of the initial HCHO concentration.

To determine the HC splits to use in the mechanism, gas chromatographic data (Dimitriades, 1969), available for six of the BOM auto exhaust samples that were run in this program, were analyzed. The average % composition of the various NMHC species determined from these data is given in Table 2. The HCs listed in this table were apportioned among the six species used in the model in the following manner:

(1) The paraffins and the non-reactive species acetylene and benzene were represented as *n*-butane. Treating these non-reactives as if they were comparable in reactivity to *n*-butane was done to compensate for the loss in reactivity that resulted from assuming that the > C_4 paraffins were only as reactive as *n*-butane.

(2) Ethylene, due to its low reactivity, was treated separately from the other olefins.

(3) Propylene and the remaining 1-alkenes, which accounted for approximately half of the 'other olefins' in the BOM exhaust samples, were represented as propylene.

(4) The 2-butenes and the other internal olefins, which accounted for the remaining half of the 'other olefins' listed in Table 2, were represented as *trans*-2-butene.

(5) Toluene was treated separately.

(6) The remaining aromatics were represented as *m*-xylene.

When apportioned in this manner, the composition of the hydrocarbon mix (expressed as % of total NMHC) was: *n*-butane 47.6%, ethylene 7.0%, propylene 9.5%, *trans*-2-butene 5.8%, toluene 11.2% and *m*-xylene 18.9%.

When this 6-component hydrocarbon mix and the chamber parameters given in Table 1 were used, reasonable fits to the observed maximum 1-h ozone concentrations were obtained for most of the 42 BOM runs that were modeled in this study. On average, O_3 was underpredicted by only 3%. Predicted maximum O_3 levels agreed within 15% of the observed values for 23 of the 42 runs; 9 runs were overpredicted by more than 15% and 10 runs were underpredicted by more than 15%.

DEVELOPMENT OF AMBIENT MODEL

To assess the effect of organic reactivity on O_3 formation, the model tested on the BOM data was adjusted to conditions that more closely approximate those found in the urban environment. The first step in this adjustment process was to select a HC composition that is representative of the present-day urban mix. HC data collected in downtown Atlanta during the summer of 1981 (Lonneman, 1982) were used in this analysis. Fourteen samples collected between 6 and 9 a.m. were averaged to obtain the % composition of the various HCs and HC classes. The results are shown in Table 3. The six HCs that were treated

Table 1. Chamber-dependent parameters used to model the Bureau of Mines chamber data

Parameter	Value
k ($NO_2 + h\nu \rightarrow NO + O$)	0.32 min^{-1}
k (chamber dilution)	3.8×10^{-4} min^{-1}
k ($O_3 \rightarrow$ Wall)	8.0×10^{-4} min^{-1}
k($N_2O_5 + H_2O \rightarrow 2HNO_3$)	0.3 min^{-1}
Rate (Wall → HCHO)	4.0×10^{-4} ppm min^{-1}
$[HONO]_i$	1% $[NO_2]_i$
$[HCHO]_i$	measured value
$[CH_3CHO]_i$	75% $[HCHO]_i$
Temperature	306.3 K

Table 2. Non-methane hydrocarbon composition of the Bureau of Mines auto exhaust samples*

Hydrocarbon	% of Total NMHC
Acetylene, benzene	9.1
Paraffins	38.5
Ethylene	7.0
Propylene	4.5
cis, *trans*-2-Butene	0.8
Other olefins†	10.0
Toluene	11.2
Other aromatics‡	18.9

*Average composition determined from gas chromatographic analysis of six auto exhaust samples (Dimitriades, 1969).

†Excluding ethylene, propylene, *trans*- and *cis*-2-butene.

‡Excluding benzene and toluene.

Table 3. Hydrocarbon composition of 6–9 a.m. samples collected in downtown Atlanta*

Hydrocarbon	% of Total NMHC
n-Butane	7.2
Ethylene	4.6
Propylene	1.2
cis, *trans*-2-Butene	1.4
Toluene	7.9
Xylenes	5.5
Σ (All other paraffins)†	54.5
Σ (All other olefins)	4.8
Σ (All other aromatics)	12.9

* Source: Lonneman (1982).
† Includes acetylene and benzene.

explicitly in the mechanism accounted for 27.8% of the total HC. The remaining 72.2% was apportioned among the six explicitly treated HCs in the same manner as that used to partition the HCs in the BOM auto exhaust samples.

To determine appropriate aldehyde levels for use in the model, formaldehyde and acetaldehyde data obtained by Corse (1981) in the 1981 Atlanta study were used. Data collected on nine days were averaged to obtain representative values for the 6–9 a.m. average HCHO and CH_3CHO concentrations. Since higher aldehydes were not measured in this study, it was assumed that these higher aldehydes were equal in concentration to acetaldehyde. Making this assumption and comparing the results to the 6–9 a.m. NMHC concentrations reported for those days (Lonneman, 1982), total aldehydes on the average were found to be 4.5% of the total NMHC. Of this total, 60% was formaldehyde. In the modeling simulations, the remaining 40% (as carbon) was taken to be acetaldehyde.

In addition to selecting new HC splits and initial aldehyde levels for use in the ambient model, the chamber-dependent parameters listed in Table 1 were either deleted or modified. Wall off-gassing of HCHO, dark decay of O_3 and $[HONO]_t$ were eliminated from the model. The pseudo-first order rate constant for the reaction of N_2O_5 with H_2O was lowered from 0.3 min^{-1} to 0.05 min^{-1}, which is the upper limit suggested by Platt *et al.* (1980) based on ambient air monitoring of the NO_3 radical in the Los Angeles air basin. Diurnally varying photolytic rates, corresponding to summer solstice at 34°N latitude, also were used. Simulations were carried out for a 12-h period corresponding to the hours 8 a.m.–8 p.m. In order to isolate the effects of organic reactivity, no dilution was used in the ambient modeling, dry deposition of pollutants was not considered and no influx of fresh precursor emissions was included. The initial conditions and other parameters used in the ambient model are summarized in Table 4.

Table 4. Ambient model parameters

Initial HC concentrations	% of NMHC
n-Butane	61.7
Ethylene	4.6
Propylene	3.6
trans-2-Butene	3.8
Toluene	7.9
m-Xylene	18.4

Other parameters
$[HCHO]_i = 0.027\ [NMHC]_i$
$[CH_3CHO]_i = 0.018\ [NMHC]_i$
$[NO_2]_i = 0.25\ [NO_x]_i$
Temp = 303 K
$k\ (N_2O_5 + H_2O \rightarrow 2HNO_3) = 0.05\ min^{-1}$
Photolysis rates: summer solstice (34°N latitude)
Simulation period: 8 a.m.–8 p.m.
No dilution
No dry deposition of pollutants
No post-8 a.m. emissions

SIMULATIONS TO ASSESS REACTIVITY

Using the ambient model described in the preceding section, simulations were conducted to assess the effect of organic reactivity on the ozone-forming potential of an urban air mass. Twelve organics were investigated in this study. Eight of these were the organics comprising the urban mix, i.e. the six hydrocarbons listed in Table 4 and the two aldehydes, HCHO and CH_3CHO. The other organics investigated were ethane, propane, methanol and ethanol. Mechanisms for these four organics were constructed by using the products and rate constants recommended by Atkinson *et al.* (1979) for the reaction of these organics with OH radicals.

Calculations were carried out in a manner that would enable one to assess the reactivity of selected organics as a function of the NMHC/NO_x ratio of the mix in which they were reacting. The ambient model and the modified OZIPP program (Whitten and Hogo, 1978) were first used to construct the 0.12 ppm O_3 isopleth over a wide range of initial NMHC and NO_x precursor concentrations. This isopleth is reproduced in Fig. 1. A number of points along the isopleth, indicated by the closed circles and corresponding to NMHC/NO_x ratios from 3 to 30, were selected. To each of the simulations that generated these points, the particular organic whose reactivity we wished to assess was added. The amount added was equivalent to 10% of the urban mix as carbon. The difference in O_3 maxima obtained in these two simulations, then, is a measure of the O_3-forming potential of the added organic.

To illustrate this method, at a NMHC/NO_x ratio of 5, 0.145 ppmC urban mix and 0.029 ppm NO_x generated 0.120 ppm O_3. When this simulation was repeated using 0.145 ppmC urban mix and 0.0145 ppmC ethylene, the maximum 1-h O_3 concentration obtained was 0.134 ppm. The change in O_3 concentration achieved upon addition of 10% ethylene was then defined as

$$\text{Change in } O_3 = \frac{[O_3\,(\text{ethylene} + \text{mix})] - [O_3\,(\text{mix})]}{[O_3\,(\text{mix})]} \times 100 = 12\%.$$

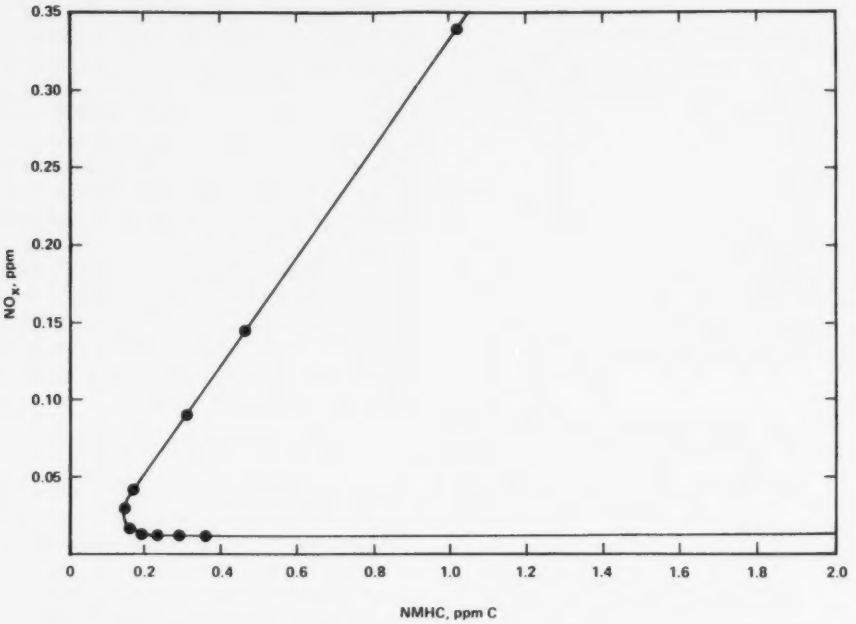

Fig. 1. The 0.12 ppm ozone isopleth as a function of initial NMHC and NO_x concentration.

These simulations were repeated for the other 11 organics and the results obtained are shown in Table 5. Of the 12 organics, ethane was the least reactive. At a NMHC/NO_x ratio of 3, O_3 increased by less than 2% when ethane was added to the mix. As the NMHC/NO_x ratio was increased, the % increase in O_3 achieved upon addition of ethane decreased. At the highest ratio investigated (NMHC/NO_x = 30), adding 10% ethane to the urban mix resulted in less than a 1% increase in O_3. Even taking into account the uncertainty of the model, it seems reasonable to conclude that ethane has little impact on the O_3-forming potential of an urban mix.

Four organics were found to exhibit moderately low reactivity throughout most of the range of NMHC/NO_x ratios that were investigated in this study. These organics were propane, *n*-butane, methanol and ethanol. At the lowest NMHC/NO_x ratio simulated in this study (NMHC/NO_x = 3), the increase in O_3 obtained when these organics were added to the mix ranged from 6 to 14%. The variation in reactivity obtained at a NMHC/NO_x ratio of 30, however, was considerably smaller, with increases that only ranged from < 1 to 2%.

All three olefins investigated in this study proved to be significantly reactive at low NMHC/NO_x ratios. At NMHC/NO_x = 3, the increase in O_3 obtained upon addition of the olefins varied from 55% for ethylene to 106% for *trans*-2-butene. At NMHC/NO_x = 30, however, the increase in O_3 ranged from 2 to only 7%, with ethylene exhibiting the greatest reactivity and *trans*-2-butene the least reactivity.

Toluene exhibited moderately low reactivity at most NMHC/NO_x ratios. *m*-Xylene, however, was found to be extremely reactive at low NMHC/NO_x ratios. At high ratios, addition of either toluene of *m*-xylene led to a decrease in O_3.

The aldehydes also were very reactive at the low NMHC/NO_x ratios, exhibiting a reactivity similar to the olefins. Formaldehyde was much more reactive than acetaldehyde at the low ratios, but the two were comparable in reactivity at the high ratios.

The most significant finding that can be gleaned from Table 5 is that the variation in reactivity at the low NMHC/NO_x ratios is significantly greater than the variation in reactivity at the high ratios. At NMHC/NO_x = 3, the change in O_3 noted upon the addition of the test organics ranged from a low of < 2% for ethane to a high of 126% for formaldehyde. At NMHC/NO_x = 30, however, the change in O_3 only varied between −8 and +7%. At high ratios, therefore, all organics exhibited comparable reactivity in contrast to the widely varying reactivity that was noted at the low NMHC/NO_x ratios.

The simulations presented in Table 5 were all conducted along the 0.12 ppm O_3 isopleth. A limited number of calculations were also performed at a much higher O_3 level to determine if the reactivity of the added test organics depends on the ozone-generating ability of the urban mix. To conduct these calculations,

Table 5. Percentage change in maximum ozone concentration when selected organics were added to the urban mix along the 0.12 ppm O_3 isopleth*

NMHC/NO_x	Ethane	Propane	*n*-Butane	Ethylene	Propylene	*trans*-2-Butene	Toluene	*m*-Xylene	Methanol	Ethanol	Formaldehyde	Acetaldehyde
3	<2	6	8	55	87	106	22	106	8	14	126	83
3.2	<2	5	8	42	61	73	18	76	6	13	79	59
3.5	<2	5	8	39	52	61	18	66	6	12	63	49
4	<2	5	8	24	28	29	13	25	6	12	23	26
5	1	3	5	12	14	14	3	9	3	7	7	12
10	1	2	3	8	10	11	−1	4	3	5	4	9
15	<1	2	2	8	8	8	−4	<1	2	3	4	8
20	<1	1	2	8	7	6	−6	−2	2	2	3	6
25	<1	1	1	7	5	4	−7	−5	2	1	3	4
30	<1	<1	1	7	3	2	−8	−7	2	1	3	3

* Amount of organic added was equivalent to 10% of the urban mix as carbon.

the 0.28 ppm O_3 isopleth was generated. The effect of adding the test organics at these NMHC and NO_x precursor levels was investigated in the same manner as that described above for the 0.12 ppm O_3 isopleth. The results are shown in Table 6. If one compares the results presented here with those given in Table 5, it can be seen that the effect of adding the various test organics was somewhat more pronounced at the low O_3 concentration than it was at the high O_3 concentration. For example, at a NMHC/NO_x ratio of 10, addition of propylene resulted in a 10% increase in O_3 along the 0.12 ppm isopleth; the addition of propylene along the 0.28 ppm isopleth led to only a 7% increase in O_3. There is some difference, therefore, but the trend is the same at both O_3 levels. Regardless of the O_3 concentration, the variation in organic reactivity is significantly greater at the low NMHC/NO_x ratios than it is at the higher ratios. The increase in O_3 noted at the lowest NMHC/NO_x ratio that yielded an O_3 maximum of 0.28 ppm (NMHC/NO_x = 3.9) ranged from 1 to 70%. The increase in O_3 obtained at a NMHC/NO_x ratio of 12, however, only varied between −6 and +7%.

DISCUSSION

The trends noted in Tables 5 and 6 support several implications regarding the reactivity of organics and the benefit in urban O_3 levels that might be achieved through the selective control of organics. At very low NMHC/NO_x ratios, there was a considerable difference in the O_3-forming potential of the various organics tested in this study. In this NMHC/NO_x regime, the selective control of the more reactive organics, such as *trans*-2-butene, *m*-xylene and the aldehydes, would be expected to result in a greater benefit on urban O_3 levels than if a control strategy involving indiscriminate control of organics were followed. This is not the case at high NMHC/NO_x ratios. As the NMHC/NO_x ratio was increased in this study, the differences in reactivity among the various organics decreased sharply. As an example, in Table 6 it was shown that the addition of *n*-butane, which is considered to be an organic of low reactivity, resulted in a 1% increase in O_3 at NMHC/NO_x = 12. The addition of *trans*-2-butene, which is considered to be an organic of exceptionally high reactivity, resulted in only a 4% increase in O_3. At very high NMHC/NO_x ratios, the differences in reactivity among the various organics decreased even further. According to Table 5, at a NMHC/NO_x ratio of 30, the addition of *n*-butane resulted in a 1% increase in O_3; the addition of *trans*-2-butene led to an increase in O_3 of only 2%.

Since the dominant loss process for most organics in the atmosphere is via reaction of the organic with OH radicals, the rate of reaction of organics with OH has been suggested as a criterion for predicting ozone formation (Winer *et al.*, 1979). The modeling results obtained in this study indicate that the organic-OH rate constant is a good measure of reactivity at low

Table 6. Percentage change in maximum ozone concentration when selected organics were added to the urban mix along the 0.28 ppm O_3 isopleth*

NMHC/NO_x	Ethane	Propane	*n*-Butane	Ethylene	Propylene	*trans*-2-Butene	Toluene	*m*-Xylene
3.9	1	5	7	46	57	65	16	70
4.5	1	4	6	26	27	29	11	26
5	1	3	4	13	14	15	2	10
10	<1	1	2	8	7	6	−5	−1
12	<1	1	1	7	5	4	−6	−3

*Amount of organic added was equivalent to 10% of the urban mix as carbon.

NMHC/NO_x ratios, but not at high ratios. Rate constants for the reaction of each of the organics investigated in this study with OH radicals are given in Table 7. Since equivalent amounts of carbon rather than molecules were added to the mix, the rate constants were divided by the number of carbon atoms contained in each organic. The resulting k_{OH}/C was then plotted against the % change in O_3 that occurred when each of the organics was added to the urban mix. The results obtained at a NMHC/NO_x ratio of 3 along the 0.12 ppm O_3 isopleth are shown in Fig. 2. As is evident from this figure, there does appear to be a relationship between the OH rate constant and the reactivity of the organics that were added to the mix at this low NMHC/NO_x ratio. Only three organics were found to deviate from the line by more than 25%. These were *trans*-2-butene, *m*-xylene and toluene. The increase in O_3 obtained upon the addition of *trans*-2-butene was significantly less than expected based on the rate of reaction of this species with OH. In contrast, the addition of *m*-xylene or toluene led to increases in O_3 that were much greater than expected. In the case of *m*-xylene, the increase in maximum O_3 was 106% compared to a predicted increase of only 32%. Similarly, the addition of toluene to the urban mix resulted in a 22% increase in O_3 instead of the predicted 10% increase.

It is probably not surprising that *trans*-2-butene was found to be less reactive than expected based on its rate of reaction with OH. Internally double-bonded olefins react extremely rapidly with O_3. Even at low NMHC/NO_x ratios, the reaction of *trans*-2-butene with O_3 competes effectively with its reaction with OH radicals, and O_3 is both produced and destroyed. Because of the importance of this O_3-consumption process, k_{OH} is not a good measure of reactivity for internal olefins.

The reason for the greater-than-expected O_3-generating ability of toluene and *m*-xylene at very low NMHC/NO_x ratios was probably due to the fact that aromatics yield highly photolyzable products such as methylglyoxal and biacetyl. These dicarbonyls photolyze at rates approximately 6–12 times greater (Plum *et al.*, 1983) than that of formaldehyde, which is the main

Table 7. Rate constants for the reaction of organics with OH radicals

Organic	k_{OH} ($ppm^{-1}\ min^{-1}$)
Ethane	4.4×10^2
Methanol	1.6×10^3
Propane	3.2×10^3
n-Butane	4.0×10^3
Ethanol	5.5×10^3
Toluene	8.9×10^3
Ethylene	1.2×10^4
Formaldehyde	1.5×10^4
Acetaldehyde	2.4×10^4
m-Xylene	3.6×10^4
Propylene	4.2×10^4
trans-2-Butene	1.0×10^5

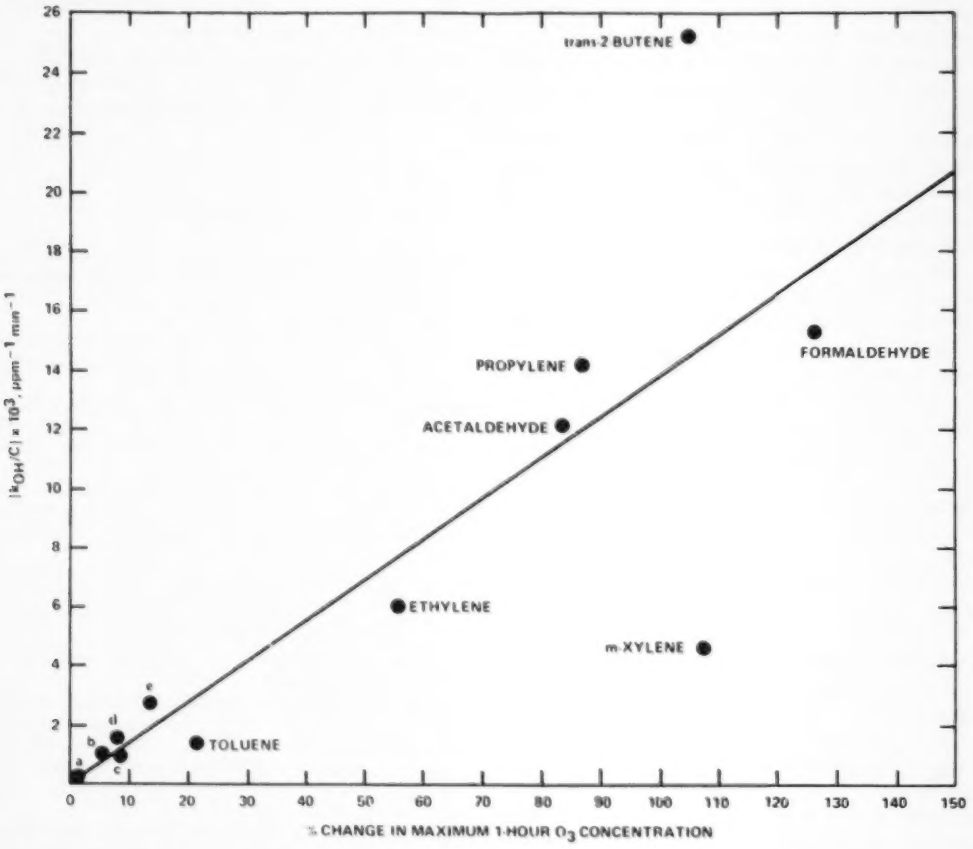

Fig. 2. Relationship between k_{OH} and % change in maximum 1-h O_3 concentration for NMHC/NO_x = 3. (Legends: a, ethane; b, propane; c, *n*-butane; d, methanol; e, ethanol.)

photolyzable product formed in most olefin and paraffin systems.

With the exception of the three organics mentioned above, the other nine organics at low NMHC/NO_x ratios behave as would be expected based on their rates of reaction with OH radicals. At high NMHC/NO_x ratios, however, there is no correlation between the predicted change in peak O_3 and k_{OH}. According to Table 5, the least reactive of the organics at high NMHC/NO_x ratios are toluene and *m*-xylene, not ethane as one would predict based on Table 7. The reactivity of the olefins also is the reverse of what one would anticipate based solely on k_{OH}, with ethylene being the most reactive and *trans*-2-butene the least reactive. Neither of these findings is surprizing. Some products formed during the oxidation of aromatic hydrocarbons, such as the cresols and the aromatic aldehydes, serve as highly effective sinks for NO_x (Killus and Whitten, 1982). At high NMHC/NO_x ratios, the system is hydrocarbon-rich and NO_x-deficient. Ozone formation is limited due to the unavailability of NO_x. Aromatics, which tend to hasten the removal of NO_x, further limit O_3 formation. The addition of aromatics at these high ratios, therefore, leads to a decrease in maximum O_3.

The fact that the order of reactivity of the olefins at high NMHC/NO_x ratios is the reverse of what one would expect is also the result of the system being hydrocarbon-rich. As the NMHC/NO_x ratio is increased, the reaction of olefins with O_3 becomes increasingly more important. As mentioned earlier, the reaction of *trans*-2-butene with O_3 is extremely rapid. Ethylene, however, reacts moderately slowly with O_3. At high HC/NO_x ratios, therefore, a larger fraction of the O_3 produced in the system is consumed when *trans*-2-butene is added to the urban mix than when ethylene is added.

SUMMARY

The goal of this study was to assess the reactivity of selected organics when present in an 'urban mix'. The extent to which this goal was achieved depends on the validity of the model used in this study. It was demonstrated that it is possible to take the detailed HC

compositional data obtained in the BOM chamber, partition these data among the six HC species used in the model and obtain results that are consistent with the data. There are, however, a number of limitations associated with the BOM data that make these data less-than-ideally suited for validating urban atmospheric chemistry models. One of these limitations stems from the fact that the BOM study used operating conditions, i.e. constant light intensity and temperature, that are significantly different from those encountered in the atmosphere. In addition, the BOM study looked at the effect of auto exhaust from a single car using a single gasoline. The effect of HC compositional changes on reactivity, therefore, was not experimentally addressed in the BOM study. Consequently, even though good agreement was obtained, there is no guarantee that the model developed in this modeling study is an accurate descriptor of chemistry in the urban environment. In addition, because the model was validated using a single auto exhaust mixture, there is no guarantee that the model can produce valid results when exercized using a different HC compositional mix as was done in this study. However, if one compares the organic composition used in the BOM modeling with the composition used in the urban mix simulations, one can see that the aromatic content of the two mixes was approximately the same, i.e. 30.1% for the BOM exhaust and 26.3% for the urban mix. The major difference in HC composition is found in the relative amounts of paraffins and olefins in the two mixes. Paraffins in the BOM model constituted a smaller portion of the mix than in the urban simulations and, conversely, the olefinic content of the BOM model was greater than the olefinic content of the urban mix. The atmospheric chemistry of paraffins and olefins is well understood; the mechanism of aromatic HC oxidation, however, is much less certain. Because the aromatic HC content of the two mixes was very similar, it is reasonable to speculate that little uncertainty in the model predictions resulted from the HC compositional shift between the BOM chamber and the urban mix.

No attempt was made in this study to generate ozone yields that would be identical to those found in the urban atmosphere given the same initial level of precursors. The simple-moving box model used in this study ignored a number of real-world phenomena such as dispersion, dry deposition of pollutants, and the influx of fresh pollutants. The O_3 yields obtained in this study, therefore, and the % changes in peak O_3 listed in Tables 5 and 6 should not be viewed as having absolute validity. The results should only be interpreted on a relative basis. When viewed in this manner, the trends exhibited in these two tables support the following conclusions:

(1) At low NMHC/NO_x ratios, organics exhibit widely varying reactivity in terms of their ability to generate O_3.

(2) At high NMHC/NO_x ratios, all organics exhibit comparable O_3-forming potential.

(3) The rate of reaction of most organics with OH radicals is a good measure of reactivity at low NMHC/NO_x ratios, but not at high ratios.

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